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Reactions of ultracold alkali-metal dimers

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We investigate the energetics of reactions involving pairs of alkali-metal dimers. Atom exchange reactions to form homonuclear dimers are energetically allowed for some but not all of the heteronuclear dimers. We carry out high-level electronic structure calculations on the potential energy surfaces of all the heteronuclear alkali-metal trimers and show that trimer formation reactions are always energetically forbidden for low-lying singlet states of the dimers. The results have important implications for the stability of quantum gases of alkali-metal dimers.

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It has recently become possible to create samples of alkali-metal dimers in deeply bound states at temperatures below 10^{-6} K [1–9]. For KRb [2] and Cs_2 [9], molecules are first formed in high-lying vibrational states by magnetoassociation and then coherently transferred to the absolute ground state by stimulated Raman adiabatic passage (STIRAP). These capabilities open up new possibilities for ultracold chemistry, for creating strongly interacting quantum gases, and for producing tunable models of important condensed-phase systems [10].

Ultracold molecules are usually confined in very shallow traps. Any collision that transfers internal energy into relative kinetic energy is likely to eject both collision partners from the trap. If both species are in their absolute ground state, inelastic collisions are impossible, but there remains the possibility of *reactive* collisions. Indeed, for fermionic $^{40}K^{87}Rb$, Ospelkaus *et al.* [11] have carried out detailed studies of the exothermic atom exchange reaction,

$$KRb + KRb \longrightarrow K_2 + Rb_2. \quad (1)$$

When all the molecules are in the same nuclear spin state, the reaction rate is strongly suppressed by the Pauli principle. However, if some of the molecules are transferred into a different spin state, the reaction proceeds very fast and the molecules are lost from the trap.

As will be seen below, atom exchange reactions analogous to (1) are energetically allowed for some alkali-metal dimers but forbidden for others. However, even when atom exchange is forbidden, there remains in principle the possibility of atom transfer reactions such as

$$KRb + KRb \longrightarrow K + KRb_2 \quad \text{or} \quad K_2Rb + Rb. \quad (2)$$

In a simple pairwise-additive model of the energetics, the reactants in such a reaction have two nearest-neighbor interactions and the products have three, so some researchers have anticipated that the trimer formation reactions would be energetically allowed. However, pairwise-additive models are known to be very poor for the quartet excited states of alkali-metal trimers [12] and are likely to be even poorer for the doublet ground states. The principle purpose of this paper is to explore the energetics of trimer formation reactions such as (2). We will demonstrate that, for singlet alkali-metal dimers in levels near the potential minimum, trimer formation reactions are in fact always energetically forbidden.

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Before proceeding to the trimer formation reactions, we briefly consider atom exchange reactions analogous to (1) for the heteronuclear dimers formed from the alkali metals Li, Na, K, Rb, and Cs. All the homonuclear and heteronuclear dimers except LiRb have been studied in detail by high-resolution spectroscopy, and dissociation energies D_e accurate to ± 1 cm^{-1} or better have been extracted as listed in Table I. The energy changes for the atom exchange reactions can therefore be calculated directly from experiment, and are summarized in Table II. The values given are taken from dissociation energies D_e measured to the dimer equilibrium geometries and so are subject to small corrections for the differences in zero-point energy between reactants and products. These corrections can be up to $+25$ cm^{-1} for LiX systems but are less than ± 2 cm^{-1} for the remainder. It may therefore be concluded that all the heteronuclear Li dimers and KRb will be subject to reactive trap loss, but all the remainder should be stable with respect to atom exchange collisions in their ground rovibronic state.

Trimer formation reactions cannot be considered in a similar way because an experimental binding energy is available only for Li_3 [27] and not for any of the heteronuclear trimers. We have therefore carried out electronic structure calculations for all the homonuclear and heteronuclear alkali-metal trimers, using the multireference average-quadratic coupled-cluster method (AQCC). All calculations used the MOLPRO package [28]. The alkali-metal atoms were described in a single-electron model and the core-valence interaction was taken into account using an effective core potential (ECP) with a core polarization potential (CPP). We used the ECPxSDF family of core potentials, developed by the Stuttgart group [29,30], with core polarization potentials based on those of Müller and Meyer [31]. We obtained modified values of the Müller-Meyer cutoff parameter (0.95 for Li, 0.82 for Na, 0.36 for K, 0.265 for Rb, and 0.24 for Cs) that reproduce the experimental bond lengths of the ground-state homonuclear alkali-metal dimers at the same level of theory. We used the uncontracted sp basis sets designed for ECPxSDF core potentials [29,30], augmented by additional s, p, d, and f functions [32]. With these polarization potentials and basis sets, we reproduced the singlet binding energies for homonuclear alkali-metal dimers with an accuracy better than 1% for Li_2, Na_2, Rb_2, and 2% for K_2 and Cs_2. The binding energies for the heteronuclear dimers are as good as for the homonuclear dimers, except for LiCs, for which the error in the binding energy was $+2.5$%.

To understand the doublet states of heteronuclear alkali-metal trimers, it is useful first to consider the homonuclear systems. The important molecular orbitals are those formed

TABLE I. Dissociation energies D_e (in cm^{-1}) for alkali-metal dimers. The quantities in parentheses are uncertainties in the final digit(s).

	Li	Na	K	Rb	Cs
Li	8516.768(8)[a]	7105.5(1.0)[b]	6216.886(100)[c]	5946(100)[d]	5875.542(5)[e]
Na		6022.0286(53)[f]	5273.62(10)[g]	5030.502(10)[h]	4954.237(100)[i]
K			4450.906(50)[j]	4217.815(10)[k]	4069.208(40)[l]
Rb				3993.47(18)[m]	3836.14(50)[n]
Cs					3649.695(2)[o]

[a]Reference [13].
[b]Reference [14].
[c]Reference [15].
[d]The binding energy for LiRb is not available from experiment, so this value is calculated using the AQCC method described in this paper.
[e]Reference [16].
[f]Reference [17].
[g]Reference [18].
[h]Reference [19].
[i]Reference [20].
[j]Reference [21].
[k]Reference [22].
[l]Reference [23].
[m]Reference [24].
[n]Reference [25].
[o]D_0 from Reference [4] and zero-point energy from Reference [26].

from the outermost s orbitals on each atom. At an equilateral triangular configuration (D_{3h} symmetry), the two highest occupied molecular orbitals of a homonuclear trimer have a_1 and e symmetry. The lowest doublet state has configuration $a_1^2e^1$. It is therefore orbitally degenerate, with ^2E symmetry, and is subject to a Jahn-Teller distortion to an isosceles geometry (C_{2v}) that splits the e orbitals into a_1 and b_2 components: the b_2 orbital has a node between the two equivalent atoms. The equilibrium structures of the homonuclear trimers all have C_{2v} geometries with ground states of $^2B_2$ symmetry.

For a heteronuclear trimer X_2Y, the symmetry is always C_{2v} or C_s. For C_{2v} geometries, the upper a_1 orbital and the b_2 orbital are close together in energy and the minimum (restricted to C_{2v}) may be on either the $^2A_1$ surface or the $^2B_2$ surface. We have therefore calculated the energy for all the heteronuclear trimers in both $^2A_1$ and $^2B_2$ states for C_{2v} geometries. Typical results are shown for Rb_2Cs in the top panel of Fig. 1. The geometry is specified by a bond length $r = r_{X_1Y} = r_{X_2Y}$ and the angle θ between the two XY bonds. It may be seen that the two surfaces intersect at an angle near $\theta = 50°$: since the two states have the same symmetry at C_s geometries, they actually intersect *only* at C_{2v} geometries, producing a seam of conical intersections there. An alternative representation of the results, for all the Rb_2X systems, is shown in the bottom panel of the figure: in this case r has been optimized to find the energy minimum for each value of θ, producing intersecting potential curves rather than two-dimensional surfaces. The minima on the two surfaces are usually close together in energy (always within 1000 cm^{-1}, but often within 200 cm^{-1}). However, the $^2B_2$ minimum is below the $^2A_1$ minimum for all the trimers except the seven heteronuclear X_2Na and Cs_2X species; for Rb_2Cs, shown in Fig. 1, the $^2B_2$ minimum is near $\theta = 63°$. The equilibrium geometries and energies for both states are provided as supplementary material [33].

TABLE II. Energy changes ΔE_2 for the reactions $2XY \rightarrow X_2 + Y_2$ (in cm^{-1}). The quantities in parentheses are uncertainties in the final digit(s).

	Na	K	Rb	Cs
Li	−328(2)	−533.9(3)	−618(200)	−415.38(2)
Na		74.3(3)	45.5(5)	236.75(20)
K			−8.7(9)	37.81(13)
Rb				29.1(1.5)

For heteronuclear trimers there is the additional possibility of distortion to a lower-symmetry C_s (scalene) geometry. We have therefore explored whether such distortions lower the trimer energies. At C_s geometries the valence orbitals formed from atomic s orbitals are all of a' symmetry, so both low-lying states have $^2A'$ symmetry and can mix. Nevertheless, in most cases it is clear whether the singly occupied orbital has bonding character (a_1-like) or antibonding character (b_2-like) between the two like atoms. For Cs_2Li, where the $^2A_1$ state was already below the $^2B_2$ state, distortion does not lower the energy and the equilibrium geometry has C_{2v} symmetry. However, for all the other systems the geometry corresponding to the $^2A_1$ minimum is in fact a saddle point on the full three-dimensional surface: for Li_2Na, K_2Na, Rb_2Na, Cs_2Na, Cs_2K, and Cs_2Rb, this simply deepens the minimum. For Li_2K, Li_2Rb, K_2Rb, K_2Cs, Rb_2Na, the distortion produces a $^2A'$ state whose absolute minimum (of C_s symmetry) is lower in energy than the $^2B_2$ state (which always retains an equilibrium geometry of C_{2v} symmetry). However, for Li_2Cs, Na_2Li, Na_2K, Na_2Rb, Na_2Cs, K_2Li, Rb_2Li, Rb_2K, and Rb_2Cs the energy gained by distortion is not enough and the $^2B_2$ state of C_{2v} geometry remains the absolute minimum.

Table III summarizes the trimer atomization energies, equilibrium geometries, and the energy change for the trimer formation reactions for all the alkali-metal trimers from Li to Cs. It may be seen that all the trimer formation reactions (from singlet dimers) are substantially endoergic. Trimer formation

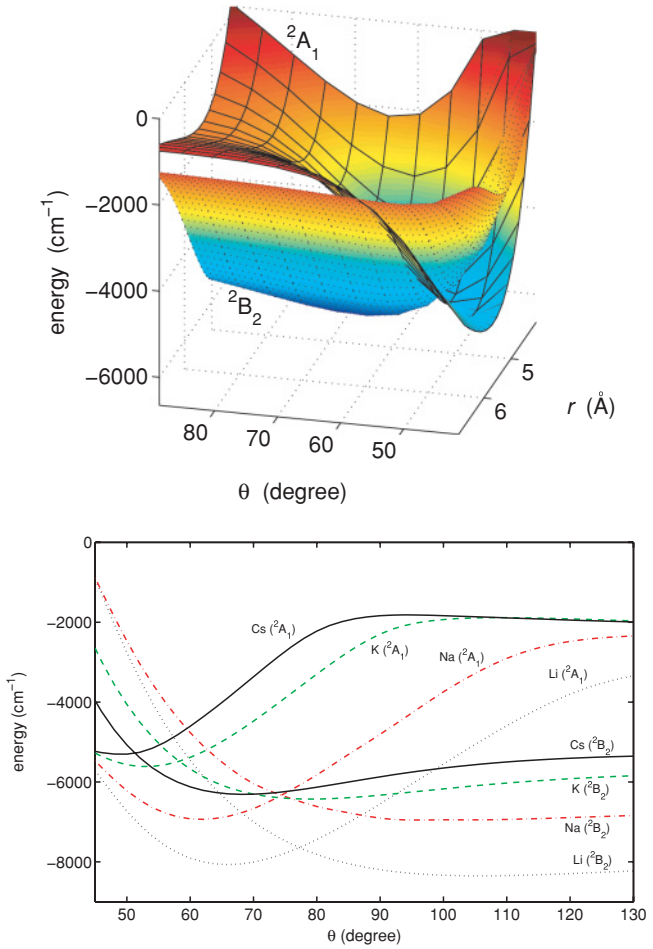

FIG. 1. (Color online) (Top) The intersecting potential energy surfaces for $^2A_1$ and $^2B_2$ states of Rb_2Cs at C_{2v} geometries, as a function of the RbCs bond length r and the bond angle θ. (Bottom) Curves for the $^2A_1$ and $^2B_2$ states of Rb_2X systems as a function of bond angle θ, with the bond length optimized at each angle. For $X =$ Li, Cs, K the minima for $^2B_2$ states are the absolute minima, while for the Rb_2Na system the absolute minimum originates from the distorted $^2A_1$ minimum geometry.

reactions will therefore not take place for alkali-metal dimers formed in singlet states near the bottom of the potential well. However, trimers may of course still be formed from dimers in triplet states, which are much more weakly bound, or from high-lying vibrational states, including Feshbach molecules.

The trimer energies are always substantially *below* the energy of any atom + diatom arrangement of the same atoms. The entrance channels of chemical reactions between alkali-metal atoms and singlet dimers are thus likely to be barrierless, as shown by Tscherbul *et al.* [34] for Rb + RbCs (though of course the reactions themselves will not always be energetically allowed). However, a full treatment of the dynamics of these reactions would require a detailed study of the potential energy surfaces for at least the two lowest-lying electronic states and the interactions between them. This contrasts with the situation for reactions involving spin-stretched states of alkali-metal atoms and triplet dimers, which have been studied using single electronic surfaces for the quartet states of the trimers [35–40].

TABLE III. Atomization energies and equilibrium geometries of the X_2Y trimers from AQCC calculations, together with energy changes ΔE_3 for the reactions $2XY \rightarrow X_2Y + Y$, obtained by combining the trimer results with dimer dissociation energies obtained with the same method. We estimate the atomization energies to be accurate to ±5%.

	X				
	Atomization energy (cm^{-1})				
Y	Li	Na	K	Rb	Cs
Li	13189	9977	8341	7982	8378
Na	11583	8113	7125	6783	7140
K	10681	7795	6258	5902	5890
Rb	10499	7649	6080	5685	5661
Cs	11073	8128	6211	5781	5494
	r_{X_1Y},r_{X_2Y},r_{XX} (Å)				
	Li	Na	K	Rb	Cs
Li	2.8,2.8,3.2	3.0,3.0,4.0	3.5,3.5,5.3	3.7,3.7,5.9	4.0,4.0,4.6
Na	3.1,3.5,2.7	3.2,3.2,4.2	3.7,4.4,4.0	4.0,4.4,4.2	4.1,4.4,4.6
K	3.5,4.3,2.8	3.7,3.7,3.9	4.1,4.1,5.2	4.2,4.2,5.7	4.4,5.5,4.8
Rb	3.6,4.5,2.8	3.8,3.8,3.8	4.2,5.3,4.1	4.4,4.4,5.5	4.6,5.5,4.7
Cs	3.8,3.8,3.1	4.0,4.0,3.7	4.2,4.5,4.9	4.6,4.6,5.5	4.8,4.8,5.7
	ΔE_3 (cm^{-1})				
	Li	Na	K	Rb	Cs
Li	3759	4145	3979	3910	3660
Na	2539	3843	3281	3287	2962
K	1639	2611	2460	2444	2264
Rb	1393	2421	2266	2295	2101
Cs	965	1974	1943	1981	1958

Our atomization energies for homonuclear systems may be compared with 13,436 cm^{-1} for Li_3 from multireference configuration interaction (MRCI) calculations [41], and 5437.1 cm^{-1} for Cs_3 from full configuration interaction (CI) calculations [42]. Our values for trimers containing Li, Na, and K also agree well (within 1000 cm^{-1}) with early CI work by Pavolini and Spiegelmann [43]. In all cases the calculations used effective core potentials similar to those in the present work.

The present results for trimer energies may be rationalized using a very simple model. In the simplest form of Hückel theory, considering only one s orbital on each atom, with a bond integral β, a homonuclear dimer in a singlet state has binding energy $2|\beta|$. An equilateral trimer has binding energy $3|\beta|$, while a linear trimer has binding energy $2\sqrt{2}|\beta|$. An atom transfer reaction such as (2) is therefore endoergic by $|\beta|$ or slightly more (i.e., by about half the dimer binding energy). This is quite different from the result predicted by pairwise additivity. However, simple orbital-based models of chemical bonding must be treated with caution for the alkali metals, because they have low-lying p orbitals that often make important contributions to bonding. Ion-pair states can also be important. Thus, while Hückel theory can be used to rationalize the results of the present work, it could not have been used to predict them. The use of high-level electronic structure calculations, as in the present work, is essential to obtain reliable conclusions.

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